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(54) **Cockle resistant inkjet paper**

(57) A minor but effective amount of a high surface area pigment having an affinity for water and a large internal pore volume is mixed with the filler pigments nor-

mally used in the paper basestock for inkjet recording sheets so as to absorb excess water from the inks during printing and provide cockle resistance to the sheets.

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**Description****Background of the Invention**

5 [0001] The present invention relates generally to the manufacture of inkjet recording paper. More particularly, the invention relates to a process for reducing or preventing cockle or wrinkling of inkjet recording paper during the printing process.

[0002] Papers for inkjet printing can be divided into two types, (a) uncoated for low quality printing, and (b) coated for high quality (usually multi-colored) printing. Uncoated papers generally contain high surface area pigments, either as fillers or added at the size press to help control dot spread. The objective is to make the sheet absorptive enough to permit rapid ink penetration, but to minimize feathering and retain good circularity of dots after printing.

10 [0003] Coated inkjet papers used for high quality multi-color printing are also required to have rapid ink absorption while still being able to dissipate the ink vehicle. However, because the ink is retained at the surface of the sheet in the coating layer, print quality is superior to that of an uncoated sheet where the ink and ink vehicle has deeply penetrated the substrate. Nevertheless, both types of inkjet recording papers must include some amount of sizing so as to keep the cellulose fibers from absorbing too much of the ink vehicle, otherwise the sheet becomes cockled or wrinkled during printing.

15 [0004] Typically, inkjet inks are aqueous based formulations which may contain from 85-95% water (by weight). Where low levels of sizing are used in the paper substrate, the cellulose fibers tend to absorb excess water which destroys the dimensional stability of the sheet and produces cockle. Where high levels of sizing are employed, the cellulose fibers absorb little or no water, so that print performance is impaired and drying times are unduly long.

20 [0005] Without subscribing to any particular theory, it is believed that the reason paper cockles is due to the absorption of water by the paper fibers which produces fiber swelling and breaking of interfiber bonds. Thus it appears that if water is allowed to penetrate a sheet with little or no sizing, the presence of the water causes the cellulose fibers in the paper to swell sufficiently to affect the dimensional stability of the sheet and produce cockle. Thus, cockle as disclosed herein refers to the swelling of paper fibers and the deformation of paper while wet with ink, which may occur immediately after printing.

25 [0006] A number of efforts have been made in the past to reduce the cockling of inkjet paper. For example, U.S. Patent No. 5,207,824 discloses the use of between 15-50% by weight of an anti-cockle agent in the ink to reduce cockle. U.S. Patent No. 5,419,644 discloses a printer control mechanism for regulating the pen-to-sheet spacing during printing to reduce cockle. Meanwhile, in U.S. Patent No. 5,431,724, the addition of a water-soluble solvent or salt to the inkjet ink is disclosed as reducing paper cockle during printing.

30 [0007] Unlike these prior art methods for reducing cockle, the present invention relies on a modification to the paper basestock used to make the inkjet sheets. Whether the inkjet sheet is coated or uncoated, it must have a high ink-absorbing capacity such that the ink vehicle is rapidly absorbed into the substrate while the images received on the recording sheet appear to be dry. This must be accomplished while still providing a high resistance to the tendency of curling and cockling. Generally, since the tendency of curling and cockling is increased with an increase in the ink absorption of the recording sheet, the requirement for enhancing the ink-absorption of the recording sheet is contradictory to the requirement of preventing the tendency of curling and cockling. Yet, in accordance with the present invention, this seemingly contradictory result is accomplished in a highly effective and cost efficient manner.

**Summary of Invention**

45 [0008] It is known that in order to achieve an inkjet recording sheet having superior performance for reproducing images, there is a conflict between obtaining maximum absorption capacity of the applied inks and ink vehicles, while retaining some dimensional stability for the sheet. U.S. Patent No. 5,213,873 describes the use of a neutral paper sheet for inkjet recording having a highly absorbent top coating containing fine silica particles for achieving superior print performance, while U.S. Patent No. 5,985,424 discloses a moderately sized sheet (Hercules size of from about 300-900 seconds), onto which there is applied both a base coating and an ink receptive top coating for achieving superior print performance. Other prior patents that disclose a relationship between ink absorption capacity and the dimensional stability of an inkjet recording sheet include U.S. Patents Nos. 4,780,356; 4,902,568; and 5,013,603. Notwithstanding these efforts and the efforts of others, there remains a need in the art to achieve the desired result in a more efficient and economical manner.

50 [0009] It is, therefore, a general object of the present invention to provide an inkjet recording sheet that has superior performance during inkjet printing.

55 [0010] It is another object of the present invention to provide a paper basestock for an inkjet sheet that has excellent dimensional stability when used with aqueous based inks.

[0011] Another object of the present invention is to reduce the cockle of the inkjet recording sheet during printing by

a cost effective modification to the paper basestock used to make the inkjet recording sheet.

[0012] These and other objects of the present invention are accomplished by substituting a minor but effective amount of a high surface area pigment having a large internal pore volume for the conventional filler materials normally used in the manufacture of the paper basestock for an inkjet recording sheet. The preferred high surface area pigments of the present invention have a specific surface area in the range of 80-650 m<sup>2</sup>/g, as compared with the specific surface area of 5-15 m<sup>2</sup>/g for conventional filler pigments. The pigments of the present invention most preferably have a bulk density of from about 0.14 to 0.26 g/cm<sup>3</sup> as compared with the bulk density of conventional inkjet pigments which range from about 0.4 to 1.0 g/cm<sup>3</sup>, and an internal pore volume as measured by an oil absorption test of from about 1.35 to 2.80 cm<sup>3</sup>/g as compared with the pore volumes of conventional inkjet pigments which range from about 0.10 to 0.50 cm<sup>3</sup>/g by the oil absorption test. The preferred substitution rate of such high specific surface area pigments for conventional pigments in the present invention is less than about 5% by weight, and on the order of about 1-5% by weight.

[0013] In this regard, the use of pigments having a high specific surface area for inkjet recording sheets either as a coating applied to the substrate or in the substrate itself is well documented in the literature as shown for example in the aforementioned U.S. Patent No. 5,013,603. However, the prior art teaches the use of such pigments in amounts greater than anticipated by the present invention, and since such pigments are generally very expensive and are not retained well during the manufacture of paper, the most economical use of such pigments in the past has been primarily in coatings applied to the paper. Now, however, it has been discovered that when a portion of the conventional pigments normally used in the manufacture of inkjet paper is replaced with a minor but effective amount of such high specific surface area pigments, the ability of the paper to absorb water from the inks without cockling is enhanced. As an example, it was found that when between 1-5% of the conventional pigments (e.g., hydrous clay, calcium carbonate and titanium dioxide) having a specific surface area of from 5-15 m<sup>2</sup>/g, was substituted with a high specific area pigment (i.e. a pigment having a specific surface area of from about 80-650 m<sup>2</sup>/g), and the papermaking furnish was sized to a level greater than 1000 seconds as measured by the Hercules sizing test, the paper so made absorbed more water in a given length of time (as measured by Cobb sizing degree), than paper containing only the conventional pigments which was sized to the same degree. The low bulk density of the high specific surface area pigments, due primarily to the large pore volume of such pigments, results in a paper basestock with reduced density and a reduced tendency to produce cockle upon printing with typical inkjet inks, while still providing enhanced print quality at a minimum ink drying time.

[0014] Thus, the subject matter of the present invention comprises a method for reducing the cockle of a paper inkjet recording sheet during inkjet printing wherein even if the paper fibers are given a high degree of sizing to prevent moisture penetration, the recording sheet is still provided with a high degree of water absorption capability by replacing a minor but effective portion of the conventional low specific surface area pigments normally used in the manufacture of inkjet paper with high specific area pigments having a large internal pore volume. The paper basestock made according to the present invention may be advantageously used as an uncoated sheet for low quality printing or it may be coated with one or more ink receptive coatings for use in making high quality, color prints. Likewise, because of the low bulk density of the added high specific area pigments, the density of the paper made is reduced as compared with the density of paper made with conventional inkjet paper pigments. The advantage of reduced density vis-a-vis improved ink absorption is fully disclosed in U.S. Patent No. 5,589,259 wherein it is noted that when the apparent density of the base paper in an inkjet recording sheet is reduced, the internal voids of the base paper is enlarged resulting in better ink absorption. Moreover, because of the reduced density of the paper basestock made in accordance with the present invention, such paper could also be advantageously used in coverstock, paperboard and other paper products benefitting from reduced density.

#### Detailed Description

[0015] The present invention will be more completely understood as a result of a review of the following Examples which describe the steps leading up to the invention. It should be understood, however, that the invention is not to be restricted or limited to the specific Examples set forth herein.

#### Example 1

[0016] In initial screening experiments, handsheets of approximately 75 g/m<sup>2</sup> were made with a blend of hardwood Kraft and softwood Kraft pulp with 0 to 4% added high surface area pigments from the families of silica, calcium silicate, and sodium aluminosilicate. It was found that the presence of the high surface area pigments, particularly those with large internal void volumes, resulted in lower paper density, preferably at levels of 2-3% filler. Two inch square samples from this initial experiment were taped to a sheet of office paper and printed blue on an HP 870 Cse printer and evaluated for cockle, with improvements seen in several samples. Formulations and results for several of the products are summarized below in Table 1.

Table 1

Initial Screening of Various Silicate Fillers			
Filler Type	Filler in Paper (%)	Density (lb/rm/cal pt)	Cockle Results
None	0	5.26 (11.6)	0
San-Sil AN-45 (silica, 60 m <sup>2</sup> /g)	1.9	4.94 (10.9)	4
	3.9	4.76 (10.5)	3
Hubersorb 250 (calcium silicate, 120 m <sup>2</sup> /g)	1.3	4.72 (10.4)	4
	2.4	4.31 (9.5)	5
Zeolex 80 (sodium aluminosilicate)	1.6	4.85 (10.7)	5
	3.1	4.85 (10.7)	5
Note: Cockle Results (0-5 worst-to-best) Density = Kg/278.7 m <sup>2</sup> /0.00254 cm (lb/3000 ft <sup>2</sup> /0.001 inch) (lb/ream/caliper point)			

## Example 2

[0017] Further development of the invention was investigated in an experiment where handsheets of approximately 170 g/m<sup>2</sup> were produced from hardwood Kraft pulp with approximately 10% total filler. A control set was manufactured with a blend of Omyafil ground calcium carbonate (GCC), No. 2 High Brightness clay, and Millenium Inorganics anatase titanium dioxide (TiO<sub>2</sub>). Experimental sets were made wherein from 2.0 to 2.4% of the conventional pigment load consisting of ground calcium carbonate, clay, and TiO<sub>2</sub> was replaced with one of three high surface area fillers: Huber Hubersorb 250 calcium silicate (surface area 120 m<sup>2</sup>/g), Degussa FK-310 silica (surface area 650 m<sup>2</sup>/g), or Speciality Minerals Jetcoat 30 precipitated calcium carbonate (surface area 80 m<sup>2</sup>/g). Both sized with a 1.81 kg/907.18 kg (4 lb/ton) of Hercules Hercon 70 AKD (alkyl ketene dimer), and unsized handsheets were made. Handsheets were calendered at 97.7 kg/linear 2.54 cm (200 pounds/linear inch) between 2 steel nips and compared for physical and optical properties. A 2.54 cm by 17.78 cm (1 inch by 7 inch) black strip was printed (using an Epson 740 inkjet printer) onto calendered paper and observed for cockle. Paper was also coated with a proprietary inkjet basecoat and topcoat, then printed with test patterns on a Epson 740 inkjet printer. Basestock made with Hubersorb or FK-310 had 5% lower density after calendering than did the control paper. The basestock made with FK-310 filler exhibited reduced cockle after printing of the black strip. Formulations and results are summarized below in Table 2.

Table 2

Finished Inkjet Basestock Properties							
Paper Set		Density (lb/rm/cal pt)	Gurley Porosity (sec)	HST (sec)	Cobb (g/m <sup>2</sup> )	Cockle Results	Silicate %
1	Sized Control	5.31 (11.7)	15	6353	29.0	2	0
2	Unsize Control	5.44 (12.0)	15	-	-	-	0
3	Sized Hubersorb	5.08 (11.2)	18	2998	37.1	4	2.1
4	Unsize Hubersorb	5.17 (11.4)	17	-	-	-	2.4
5	Sized FK 310	5.13 (11.3)	14	2799	47.0	4	2.0
6	Unsize FK 310	5.08 (11.2)	15	-	-	-	2.0
7	Sized Jetcoat	5.40 (11.9)	17	2728	43.5	2	0

Table 2 (continued)

Finished Inkjet Basestock Properties							
Paper Set		Density (lb/m/cal pt)	Gurley Porosity (sec)	HST (sec)	Cobb (g/m <sup>2</sup> )	Cockle Results	Silicate %
8	Unsize Jetcoat	5.442 (12.1)	18	-	-	-	0
Note: Control: 45% Ground Calcium Carbonate (Specific Surface Area 11 m <sup>2</sup> /g) 45% Clay (Specific Surface Area 12 m <sup>2</sup> /g) 10% TiO <sub>2</sub> (Specific Surface Area 12 m <sup>2</sup> /g) Cockle Results (0-5 worst-to-best) Density = kg/278.7 m <sup>2</sup> /0.00254 cm (lb/300 ft <sup>3</sup> /0.001 inch) (lb/ream/caliper point)							

[0018] In another experiment using lightweight handsheets having a basis weight of about 130 g/m<sup>2</sup> (a more demanding test for cockle), samples were prepared with 0, 2% and 4% addition of Degussa FK-310 silica pigment and sized with a combination of AKD internal size and a surface application of SMA and starch. The pulp, control fillers and additives were the same as in Example 2 above. The results are shown in Table 3 below.

Table 3

Cockle Results			
Pigments	HST (sec)	Cobb (g/m <sup>2</sup> )	Cockle
Control	3521	33	2
2% FK-310	1641	36	3
4% FK-310	547	54	4

[0019] Examples of conventional pigment filler materials useful in inkjet recording sheets include inorganic pigments such as talc, clay, kaolin, diatomaceous earth, calcium carbonate, precipitated calcium carbonate, calcium sulfate, barium sulfate, titanium dioxide, zinc oxide, zinc carbonate, aluminum silicate, calcium silicate, aluminum hydroxide, aluminum oxide, synthetic amorphous silica, colloidal silica, and/or organic pigments such as urea resin pigments, plastic pigments, etc., if desired, all having a fairly low specific surface area on the order of from about 5-15 m<sup>2</sup>/g. Meanwhile, examples of high specific area pigments useful in the present invention include Huber Hubersorb 250 calcium silicate (specific surface area 120 m<sup>2</sup>/g); Degussa FK-310 silica (specific surface area 650 m<sup>2</sup>/g); and, Speciality Minerals Jetcoat 30 precipitated calcium carbonate (specific surface area 80 m<sup>2</sup>/g). These and other silica based pigments which have a low bulk on the order of from about 0.14 to 0.26 g/cm<sup>3</sup> and a large internal pore volume as measured by an oil absorption test of from about 1.35 to 2.80 cm<sup>3</sup>/g, e.g., the Dibutyl Phthalate (DBP) absorption test, are preferred for use in the present invention.

[0020] While it is apparent that the invention as disclosed herein is well adapted to fulfill the objects stated hereinbefore, it will be appreciated that numerous modifications and other embodiments may be devised by those skilled in the art. It is intended, therefore, that the appended claims cover all such modifications and embodiments as fall within the spirit and scope of the invention.

#### Claims

1. The method for reducing the cockle of paper based inkjet recording sheets during printing while providing high absorption capability of applied inks and low drying time comprises adding to the papermaking furnish used to prepare the inkjet recording sheet a minor but effective amount of a high surface area pigment having a large internal pore volume for absorbing the excess water in the applied inks while simultaneously providing sufficient size to the furnish to render the pulp fibers in the furnish water resistant.
2. The method of claim 1 wherein the high surface area pigment has a specific surface area within the range of from about 80-650 m<sup>2</sup>/g.

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3. The method of claim 2 wherein the high specific surface area pigment comprises from about 1-5% of the filler pigment added to the papermaking furnish.
4. The method of claim 3 wherein the papermaking furnish has a size of greater than about 1000 seconds as measured by the Hercules Size Test.
5. The method of claim 4 wherein the high specific area pigment has an internal pore volume greater than about 1.35 cm<sup>3</sup>/g as measured by an oil absorption test.
6. The method of claim 5 wherein the high specific area pigment is selected from the group consisting of silica, silicates and aluminosilicates.
7. An inkjet recording sheet having improved cockle resistance comprising a sized paper basestock having a size greater than about 1000 seconds as measured by the Hercules Size Test and a total filler content of at least about 10%, wherein from about 1 to 5% of the total filler content consists of a high surface area pigment having a specific surface area of from about 80-650 m<sup>2</sup>/g, an internal pore volume as measured by an oil absorption test greater than about 1.35 cm<sup>3</sup>/g, and a bulk density of from about 0.14 to 0.26 g/cm<sup>3</sup>.